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SHORT COMMUNICATION

Absorption spectra of an electrochromic window based on molybdovanadophosphoric acid, Prussian Blue and a solid polymer electrolyte

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1. Introduction

Several electrochromic materials have been investigated for possible use in 'smart window' application [1–5] and colour switching displays [6–8]. Smart windows may elegantly contribute to energy savings in buildings by dynamic control of light transmission.

Transmission spectra for an electrochromic window based on tungsten oxide (WO_3) and Prussian Blue, using a Li^+ doped polymer electrolyte, oxymethylene polyoxyethylene as electrolyte, in the 300–850 nm wavelength region have been studied by Habib *et al.* [9]. Reflection spectra for phosphotungstic acid in the 400–1000 nm wavelength region are given by Tell [10]. Maheswari [11] reported the electrochromic behaviour of phosphotungstic acid in an aqueous solution. In this work, we have extended the phosphotungstic acid to molybdovanadophosphoric acid (MVPA).

We have studied an electrochromic window with MVPA and PB deposited on ITO coated glass plates, and with a Li^+ doped oxymethylene polyoxyethylene (OMPE) as a solid polymer electrolyte. As shown in Fig. 1, the total glass sandwich becomes 'glass/ITO/MVPA/OMPE/PB/ITO/glass'.

2. Experimental details

PB films were deposited electrochemically at a constant current of $7\,\mu A\,cm^{-2}$ for 10 min on ITO glass plates ($100\,\Omega\,cm^{-2}$) from an equivalently mixed solution of 0.01 M $FeCl_3$ and 0.01 M $K_3Fe(CN)_6$. Molybdovanadophosphoric acid ($H_5PMo_{10}V_2O_{40}$) was prepared by Tsigdinos and Hallada's method [12]. MVPA films were fabricated on an ITO glass substrate by spin-coating a solution of MVPA in acetonitrile.

The solid polymer electrolyte was made by using a similar method to that described by Habib [9]. The OMPE polymer electrolyte was sandwiched using a Teflon spacer (0.1 mm thickness) between a MVPA film and PB film (each about 4 μm thick) previously made on ITO glass substrates. The components of the cell were held together by a set of metal clips across the ITO–glass substrates.

Electrochemical measurements were performed with M273(EG&G) potentiostat/galvanostat. A UV-3100(Shimadzu) recording spectrophotometer was used for the u.v.–v.i.s.–n.i.r. spectra measurements. The assembled PB–MVPA cell was placed in the spectrophotometer sample chamber and the electrodes were connected to the electrochemical equipment outside the chamber. For electrochemical measurements involving a single film (MVPA-only or PB-only), a Ag/AgCl reference electrode and platinum counter electrode were used. For the assembled MVPA–PB cell, no reference electrode was used and the potential was applied between the MVPA and the PB electrode. Voltages of the cell are reported as applied to the MVPA electrode against the PB electrode. The absorption spectra were recorded under potentiostatic control and, in order to stabilize the electrochromic films, the window was held at a constant potential for 2 min before recording the absorption spectra.

3. Results and discussion

Cyclic voltammograms ($5\,mV\,s^{-1}$) of the electrochromic window in the potential region +1.0 ~ −1.8 V are shown in Fig. 2. A negative voltage means that MVPA is reduced while PB is oxidized, and the window attains a blue colour. By cycling between +1.0 and −1.8 V the colour switches from pale yellow to dark blue. The schematic cell reaction in the window, also indicating the colour changes, can be written as

$$\begin{aligned} &LiKFeFe(CN)_6 + \underset{\text{yellow}}{MVPA} + xe^- + xLi^+ \\ &\longrightarrow Li_{1+x-y}\,\underset{\text{blue}}{MVPA} + Li_yKFeFe(CN)_6 \end{aligned} \tag{1}$$

where x is the number of cations and electrons transferred in the reaction. This cell reaction is oversimplified and does not include the necessary proton transfer in MVPA during the redox process.

Absorption spectra in the 350–950 nm wavelength region for the window at different applied potentials are shown in Figs 3 and 4. Figure 3 depicts the absorption through the entire window, while the spectrum of only the 'glass/ITO/OMPE/ITO/glass' reference is shown in Fig. 4. Absorption spectra in the

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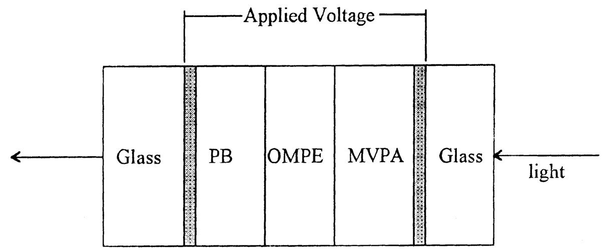

Fig. 1. Schematic diagram of the EC window.

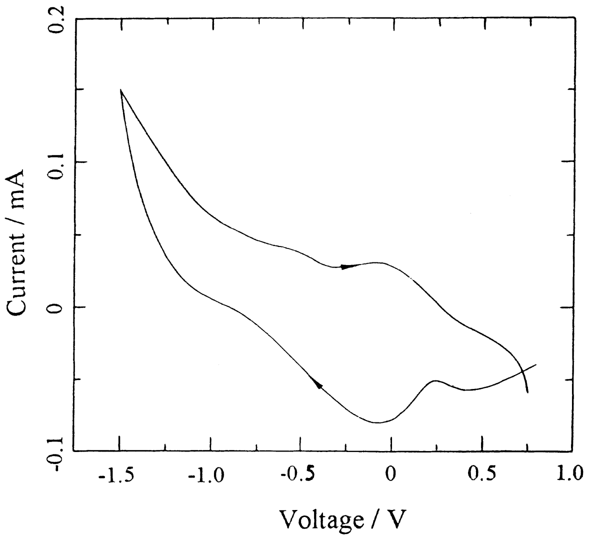

Fig. 2. Cyclic voltammograms of the EC window (scan rate: 5 mV s^{-1}).

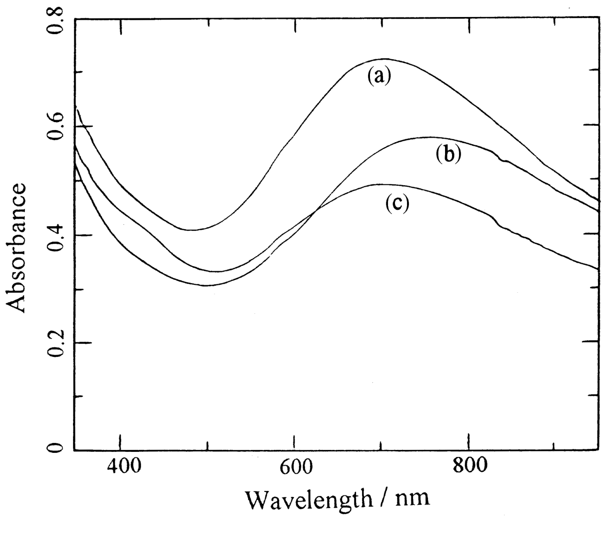

Fig. 3. Absorbance vs. wavelength in the EC window at −1.5 V (a), 0 V (b), and +1.0 V (c).

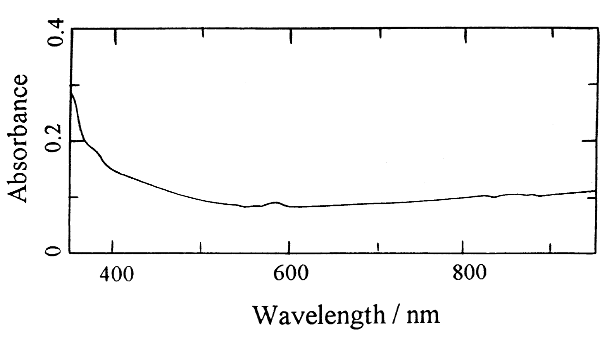

Fig. 4. Absorbance against wavelength in the reference.

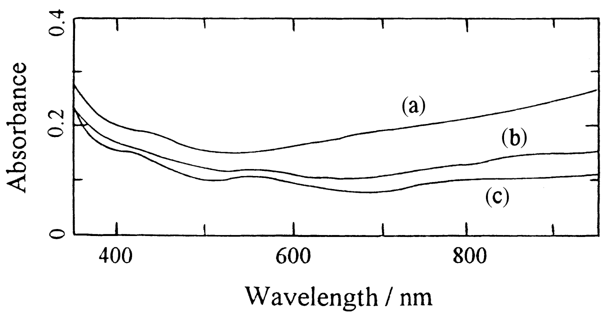

Fig. 5. Absorbance against wavelength of MVPA film only at −1.5 V (a), 0 V (b), and +1.0 V (c).

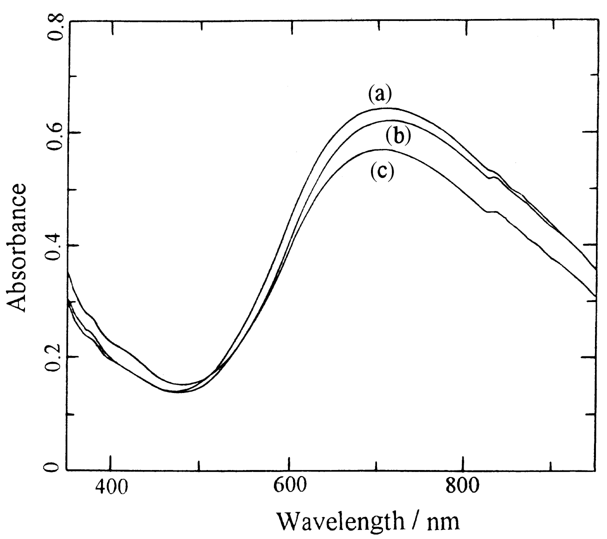

Fig. 6. Absorbance against wavelength of PB film only at +0.6 V (a), 0 V (b), and −0.3 V (c).

350–950 nm wavelength region for the MVPA and PB only at different applied potentials are shown in Figs 5 and 6. In Fig. 3, the absorbance at 1.0 V (curve c) is more than that at 0 V (curve b) in the range of 350–650 nm. This is believed to be due to the greater absorbance of the reduced species of MVPA. The window consists of the PB electrode and the MVPA electrode, so the absorbance of the window is the sum of that of the two electrodes. In the case of the window at +1.0 V, the MVPA electrode is at reduced state and the PB electrode is at oxidized state. From Fig. 3 and Figs 5 and 6 it can be seen that the degree of light modulation of the electrochromic window in the 400–850 nm region by applying a voltage between 1.0 and 1.5 V is good, for example, a change in absorbance from 0.73 (−1.5 V) to 0.48 (+1.0 V) at 700 nm.

4. Conclusion

An electrochromic window consisting of molybdovanadophosphoric acid, Prussian Blue, the solid polymer electrolyte oxymethylene polyoxyethylene and glass plates coated with indium-tin-oxide shows good properties for light modulation in the 400–850 nm wavelength region.

Acknowledgements

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